250 Course on Surface Science (Fall 1999)

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Topics to be covered:

Ch.1   Thermodynamics of surfaces

The surface tension concept. Droplets and bub-bles

Microscopic wetting theories. Shape of droplets

Equilibrium shape of crystals. Wulff's theorem

Faceting of non-vicinal surfaces

Roughening transition

Premelting

Ch.2   Experimental topics: Ultra High Vacuum (UHV). Gas collisions, mean free path. Preparation of surfaces: polishing, sputtering, annealing. Electrochemistry. Chemical preparation.

Ch.3   Surface tools and spectroscopies:

Composition: Auger, XPS, Ion Scattering, TPD, SIMS

Ch.4   Crystallography: LEED, Grazing X-rays, Photoelectron diffraction, forward focusing, etc.

Ch.5   Electronic structure: Photoelectron ARUPS, NEXAFS

Ch.6   Vibrations and Phonons: IR, HREELS, He scattering, Raman, SFG

Ch.7   Real space techniques: STM. Principles, local electronic structure.

Ch.8   Real space techniques: AFM. Principle. Contact and non-contact operating modes.

Other chapters: semiconductor surfaces and interfaces, atomic manipulation, crystal growth, catalysis (chemisorption), environmental science.

Books and papers:

Physics at Surfaces   Zangwill (Cambridge)
Physical Chemistry of Surfaces   Adamson (Wiley)
Intermolecular and Surface Forces   Israelachvili (Academic Press)
Volume 5 of Landau and Lifshitz
Surface Forces   B.V. Derjaguin, N.V. Churaev and V.M. Muller. Plenum
Statistical Physics of Crystal Growth   Yukio Saito, World Scientific
….. more to be added …………….

Ch. 1 THERMODYNAMICS OF SURFACES

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1. Review of thermodynamics

a) Principles

- First principle (only reversible processes will be considered.): $\bar{\delta}Q = \delta U + \bar{\delta}W$

  ($\bar{\delta}$ symbols meaning non-exact differentials), Q heat, W mechanical or other work.

- Second principle: $\delta S = \dfrac{\bar{\delta}Q}{T}$ (for reversible processes; > for irreversible ones)

- Together they lead to the fundamental relation:

$$T\delta S = \delta U + p\delta V + \bar{\delta}W \qquad (1)$$

$\bar{\delta}W$ stands for any other work performed by the system.

The additivity principle (if the system doubles its size, or its extensive parameters, the energy doubles also), implies that the energy U(N,V,S) is an homogeneous function of the first order:

$$U(\lambda N, \lambda V, \lambda S) = \lambda U(N,V,S)$$

This leads to the Euler equation, obtained by differentiating this expression with respect to λ, then making $\lambda = 1$, integrating and using the third principle S(T=0) = 0:

$$U = \mu N - pV + TS \qquad \text{(Euler eq.)}$$

Where $\mu = \partial U/\partial N$; $p = -\partial U/\partial V$; and $T = \partial U/\partial S$, are the three conjugate variables of N, V and T, the normal variables of the energy, as a thermodynamic potential.

The differential of Euler eq. together with the fundamental eq. (1), leads to the Gibbs-Duheim equation:

$$SdT - Vdp + Nd\mu = 0 \qquad (2)$$

b) Thermodynamic potentials

       The most common thermodynamic potentials are, in differential and integral form (repeated indices meaning summation over all types of particles):

Energy $U(S, V, N_j)$: $dU = TdS - pdV + \mu_j dN_j$ $U = TS - pV + \mu_j N_j$

Helmholtz free energy $F(T, V, N_j)$: $dF = -SdT - pdV + \mu_j dN_j$ $F = U - TS = \mu_j N_j - pV$

Gibbs free energy $G(T, p, N_j)$: $dG = -SdT + Vdp + \mu_j dN_j$ $G = U - TS + pV = \mu_j N_j$

Omega potential $\Omega(T, V, \mu_j)$: $d\Omega = -SdT - pdV - N_j d\mu_j$ $\Omega = F - G = -pV$

       When should we use one potential or another? Any potential can be used to define equilibrium, by the condition of minimum (first derivative = 0, second >0). However it is best to use the potential whose natural variables remain constant. For example, $\Omega(T, V, \mu_j)$ is to be used in open systems (with V and T constant), where N_j varies but where μ_j stays constant.

2. Surface tension

       The surface tension γ is defined as the work done to reversibly create a unit area of surface between two phases:

$$dW = \gamma \, dA \qquad (3)$$

A = surface area. The term γA (which is similar to the $-pV$ term), should be added to the thermodynamic potentials defined above when there is a surface.

       The useful thermodynamic potential here is Ω, since in creating a surface at constant T and V, the other variables can change: p, for curved surfaces and N_j, the number of particles. However in equilibrium μ will stay constant. In such a process:

$$d\Omega = \gamma \, dA \qquad (4)$$

3. Definition of the surface of single substance

In general the properties of the particles in a medium change as they get close to the interface between two phases. This happens over a region with dimensions equal to the range of interaction forces, inside each phase. In this surface region the properties change from those of bulk phase 1 to bulk phase 2. Arbitrarily three regions can be defined: bulk 1, bulk 2 and surface, with volumes V_1, V_2, and V_s such that of course $V = V_1 + V_2 + V_s$. Similarly, any other magnitude such as energy will be written $U = U_1 + U_2 + U_s$, etc. However, following Gibbs, the surface can be defined mathematically as the plane separating phase 1 and 2 of the same substance, such that:
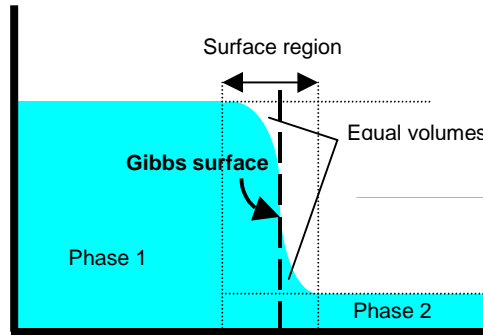
(i) $V = V_1 + V_2$, (with $V_s = 0$); and

(ii) $n_1V_1 + n_2V_2 = N$, where n_1 = density of particles in phase 1 and n_2 = density of particles in phase 2.

By definition, there are no particles at the surface: $N_s = 0$. This choice is no longer possible with more than one component, for example in solutions, as we shall see later.

At T and μ constant, we have: $\Omega = \Omega_v + \gamma A$

where Ω_v is the sum of Ω_1 and Ω_2. The surface entropy is:

$$S_s = -\frac{\partial \Omega_s}{\partial T} = -A.\frac{d\gamma}{dT} \qquad (5)$$

The derivative is total instead of partial because γ does not depend on μ, because Ω_s does not depend on μ either. This is because of our choice of the surface, with $N_s = -\partial\Omega_s/\partial\mu = 0$.

The free energy $F = \Omega + \mu N$, has a surface part $F_s = \gamma A$, because again $N_s = 0$. The energy to create a surface is:

$$U_s = F_s + TS_s = (\gamma - Td\gamma/dT).A \qquad (6)$$

The heat adsorbed to create the surface is:

$$Q = T(S_{s2} - S_{s1}) = -T.d\gamma/dT.(A_2 - A_1) \qquad (7)$$

4. Surface of heterogeneous systems: solutions

We can define the surface as before with respect to the solvent:

$$V = V_1 + V_2, \quad \text{and} \quad N_1 + N_2 = N, \quad \text{with} \quad N_s = 0$$

with capital N's standing for solvent number of molecules. However, once this choice is made there is no more freedom left and in general we cannot make $N'_s = 0$, (primed letters referring to the solute). So we will have $N'_s = N' - N'_{vol}$, where N'_{vol} represents the extrapolated number of solute molecules assuming the bulk densities propagate up to the mathematical surface. If $N'_s > 0$ we talk of positive adsorption, and negative if $N'_s < 0$. Now Ω_s and γ, depend on two variables: T and μ', the solute chemical potential. We have then:

$$N'_s = -\partial\Omega_s/\partial\mu' = -A. (\partial\gamma/\partial\mu')_T \qquad (8)$$

In principle the derivative is to be taken along the phase equilibrium line, where the pressure is also changing; however, since the liquid is hardly affected by this,

we can ignore the condition and assume p = constant. Since μ' depends on the concentration, so does γ.

$$N'_s = -A. \left(\partial\gamma/\partial c\right)_T.\left(\partial c/\partial\mu'\right)_T \qquad (9)$$

Since $\left(\partial c/\partial\mu'\right)_T > 0$ always, we obtain the result that substances that increase the surface tension show negative adsorption while those that decrease γ, segregate. This result is quite intuitive. If the solution is diluted, the dependence of μ' on c is of the form:

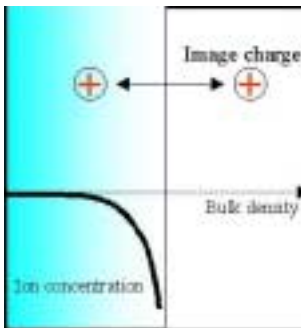$$\mu' = \mu'_0 + kT.\log c \qquad (10)$$

so that $\left(\partial c/\partial\mu'\right)_T = c/kT$, and $\qquad N'_s = -Ac/kT. \left(\partial\gamma/\partial c\right)_T \qquad (11)$

The change of γ with c, for diluted solutions is $\gamma = \gamma_0 + \gamma_1.c + \ldots$ One obtains then the interesting result:

$$\gamma_0 - \gamma = \theta.N_o.kT \qquad (12)$$

where θ is the surface coverage $N'_s/ (N_oA)$, N_o being the surface atom density ($\sim 10^{15}/cm^2$, for a solid or liquid).

5. Strong electrolites (ionic solutions)

Because of their charge, ions in solution experience two potentials as they approach the surface. One is from the electrostatic force due to the image charge. This force is repulsive for ions in water, with air on the other side, since water is dielectrically denser. The other term is from the electrostatic forces due to all other ions in the solution:

$$E_j = \frac{\varepsilon - 1}{\varepsilon(\varepsilon + 1)} \times \frac{e^2 z_j^2}{4x} + e z_j.\phi(x) \qquad (13)$$

Charge neutrality implies that $c_j z_j = 0$ (sum of charges of each species times concentration). $e^2 \equiv q_e{}^2/(4\pi\varepsilon_o)$, in SI units.

Exercise: find the order of magnitude of E_j

With this energy we can calculate the density distribution. From Boltzman statistics, the concentration near the surface differs from the bulk value c_j by the factor $\exp(-E_j/kT) \approx 1-E_j/kT$, since the energy E_j is very small. So the surface excess of component j is:

$$N_{S,j} = -\frac{A.c_j}{v.kT}\int_0^\infty E_j(x)dx \qquad (14)$$

v is the molecular volume of the solvent so that A.dx/v is the number of solvent molecules, which multiplied by c_j gives the number of solute molecules.

To calculate the surface tension, we use the Gibbs-Duheim expression (2), with p and T constants (we have to add Adγ to (2)):

$$Ad\gamma + N'_{S,j}d\mu'_j = 0$$

together with the assumption of dilute solution, which means $\mu'_j = \mu'_{j,0} + kT\log c_j$
So we have:

$$Ad\gamma = -kTN'_{S,j}dc_j/c_j \quad \text{(reminder: repeated indices = summation)}$$

Substituting the expression for N'$_{S,j}$:

$$d\gamma = \frac{1}{v}dc_j\int_0^\infty E_j(x)dx \qquad (15)$$

[this can also be obtained directly by comparing the expression for N'$_{S,j}$ with (11)].

In the expression for $E_j(x)$, the last term disappears after summation, due to charge neutrality. The integration should be carried out between a lower limit

distance of atomic dimensions from the surface (a_j), and an upper limit of the order of the Debye length, $\lambda_{D,j}$. One obtains:

$$dy = \frac{(\varepsilon - 1)e^2}{4\varepsilon(\varepsilon + 1).v} \log \frac{\lambda_{D,j}}{a_j} d(z_j^2 c_j) \qquad (16)$$

Since $\lambda^{-1}_{D,j} \propto \sqrt{z_j^2 c_j}$, this differential equation can be integrated to give:

$$\gamma - \gamma_0 = \frac{(\varepsilon - 1)e^2}{8\varepsilon(\varepsilon + 1)v} \times z_j^2 c_j \log \frac{z_j^2 b_j}{z_k^2 c_k} \qquad (17)$$

where the b_j's are constants.

The surface tension of a strong electrolyte always increases, since b >> c.

This can be seen by evaluating the constants: Debye length $\lambda_{D,j}$ = $\sqrt{\dfrac{kT}{8\pi e^2 c_j}}$ so

that, at RT, one gets: $b_j \sim 2.3 \times 10^{18}$ m$^{-3/2}$, which is very large compared with the highest possible density (a solid) $[c_{solid}]^{1/2} \sim 3.5 \times 10^{14}$ m$^{-3/2}$.

6. Droplets and bubbles: nucleation

When a vapor is cooled down, eventually the pressure will become saturating and droplets of the liquid phase will condense. If a liquid is heated, at some point bubbles will form. These phenomena result in the creation of a
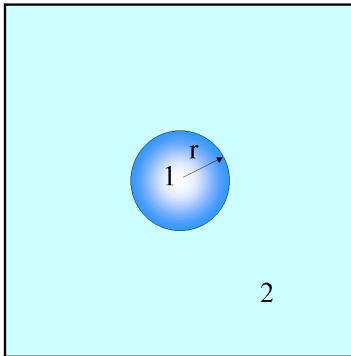
surface that costs energy and this can delay the formation of nuclei. The vapor will be supercooled and the liquid superheated. Preexisting nuclei (dust, ions, surfaces) may provide this initial nuclei.

Lets consider two phases 1 and 2, separated by a surface of area A, in equilibrium. Since μ and T are constant, we use the Omega potential:

$$\Omega = -p_1 V_1 - p_2 V_2 + \gamma A \qquad (18)$$

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Since $V_1 + V_2$ = constant, $d\Omega = -(p_1 - p_2)dV_1 + \gamma dA = 0$, since we are in equilibrium. For a planar surface this means $p_1 = p_2$, since $dA = 0$.

For curved surfaces, like in a droplet, the pressures are not the same because in moving the curved surface, it changes dimensions and energy (γ) is spent. However, $\mu_1(p_1,T) = \mu_2(p_2,T)$. Since $V_1 = 4/3\pi r^3$, and $A = 4\pi r^2$, we obtain:

$$p_1 - p_2 = 2\gamma/r \qquad (19)$$

This is the classical formula of capillary phenomena. r is negative for bubbles. The increase (or decrease) in pressure due to γ is called Laplace pressure. If instead of a droplet we have a cylinder or any other shape characterized by local curvature radii r_1 and r_2, the formula is:
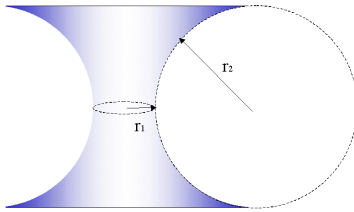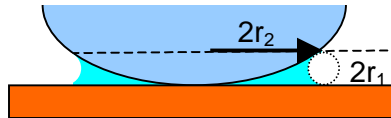

$$p_1 - p_2 = \gamma(1/r_1 + 1/r_2) \qquad (20)$$

One of these could be negative, like in the neck of the figure. In this case:

$$p_1 - p_2 = \gamma(1/r_1 - 1/r_2) \qquad (21)$$

Exercise: calculate the force due to the Laplace pressure as a result of capillary condensation around a tip in contact with a surface (assume perfect wetting). Answer: since $r_1 >> r_2$, $\Delta p = -\gamma / r_2$ and $F = \Delta p \times area = -4\pi\gamma R$, where R is the tip radius.

Next we want to calculate the difference between these pressures and the equilibrium pressure over a flat surface, p_o, i.e., the saturation vapor pressure.

We start with $\mu_1(p_1,T) = \mu_2(p_2,T)$ and the relations $\mu(p,T) = \mu(p_o,T) + kT\log(p/p_0)$. For the vapor in equilibrium with the flat surface we also have $\mu_1(p_0,T) = \mu_2(p_0,T)$. Combining we get:

$$\mu_1(p_1,T) - \mu_1(p_0,T) = \mu_2(p_2,T) - \mu_2(p_0,T) \qquad (22)$$

and for small differences in pressure, by series expansion and using the equality: $v = -\partial\mu/\partial p$, we get:

$$v_1\delta p_1 = v_2\delta p_2, \qquad (23)$$

where $\delta p_j \equiv p_j - p_0$. Since $\delta p_1 - \delta p_2 = 2\gamma/r$, substituting we obtain:

$$\delta p_1 = \frac{2\gamma}{r} \cdot \frac{v_2}{v_2 - v_1} \approx \frac{2\gamma}{r}, \qquad \text{since } v_2 \gg v_1 \qquad (24)$$

$$\delta p_2 = \frac{2\gamma}{r} \cdot \frac{v_1}{v_2 - v_1} \approx \frac{2\gamma}{r} \cdot \frac{v_1}{v_2}$$

Using the perfect gas equation: $pV = NkT$, we have $v_2 = kT/p_2 \approx kT/p_0$, so:

$$\delta p_{vap} = \frac{2\gamma v_{liq} p_0}{rkT} \qquad (25)$$

which gives the increase in vapor pressure over a spherical droplet, relative to that on the flat surface. Therefore, if there is a collection of droplets, there can be no equilibrium. The big ones will grow at the expense of the small ones, since these would require higher vapor pressure around them. This is akin to the so called Ostwald ripening.

For very small droplets, we cannot use the approximation $v_1\delta p_1 = v_2\delta p_2$, since δp_2 can become quite large. We then need to use the unexpanded form of $\mu(p,T) = \mu(p_o,T) + kT\log(p/p_0)$. With this we get:

$$\log \frac{p_{vapor}}{p_0} = \frac{2\gamma v_{liq}}{rkT} \qquad (26)$$

Example: for water $\gamma = 73$ mJ/m^2. At RT, the increase of the vapor pressure over a droplet of $r = 1000$ Å is 1% of the p_o. If the radius is 100 Å, the increase is 10%, and if $r = 10$ Å, it increases by a factor 2.7! That is why condensation will not occur even if equilibrium dictates it should (supercooling). This is the problem of nucleation.

Let's consider the energy cost of nucleating a drop (or bubble) out of equilibrium, ($\mu_1 \neq \mu_2$) as a result of a fluctuation. The free energy will increase by the amount:

$$\Delta F = \Delta \Omega + \Delta \mu N = \gamma A + (\mu_1 - \mu_2)N = 4\pi r^2 \gamma + (\mu_1 - \mu_2)4/3\pi r^3/v_{liq} \quad (28)$$

If $\mu_1 > \mu_2$, then of course no condensation can occur. If the vapor is supersaturated, then $\mu_1 < \mu_2$, and the cubic term is negative. The graph looks like:
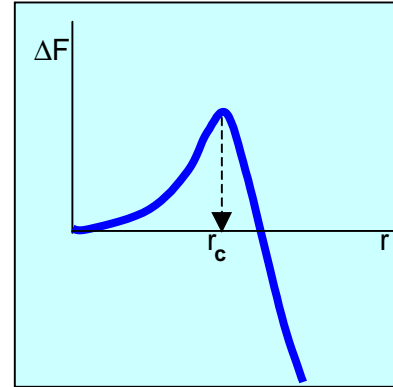
A density fluctuation must generate a nucleus of radius larger than r_c to nucleate a drop. Differentiating we find:

$$r_c = 2\gamma v_{liq}/(\mu_2 - \mu_1) \qquad (29)$$

7. Macroscopic capillarity phenomena

The surface tension of liquids has familiar consequences on the contact geometry between liquids and solids or other liquids. In the absence of contact, the free liquid adopts a spherical shape, since this minimizes the area and thus the surface energy (drops and bubbles). If the surface tension of the liquid-vapor interface (γ) is smaller than the difference between that of the solid-vapor (γ_{sv}) and the solid-liquid (γ_{sl}), then the liquid is said to wet the surface and a flat film

will forms, because $\gamma + \gamma_{sl} < \gamma_{sv}$. If the sum is larger, energy is minimized by forming droplets that only partially cover the surface. The quantity $S = \gamma_{sv} - \gamma_{sl} - \gamma$ is called the spreading coefficient. For S>0, the liquid spreads flat. For S<0, droplets form that adopt spherical-cap shapes, with a contact angle φ.
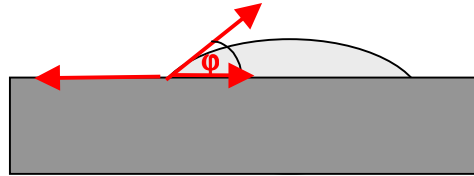
The value of φ is determined by the condition of mechanical equilibrium of line forces (the contact line does not advance or recede). Since the forces are tangent to the corresponding interface planes and perpendicular to the line, we have:

$$\gamma_{sv} = \gamma . \cos\varphi + \gamma_{sl}^{-} \qquad (30)$$

This is called the Young equation. For shallow droplets, (small contact angles) it can be rewritten as: $S = -1/2\gamma\varphi^2$. We will use this expression later on.

The same result can be obtained by minimizing the total free energy as a function of droplet shape at constant volume. The minimization also shows that the shape is a spherical cap. This is of course neglecting other forces, in particular gravity. We shall come back to this subject later on.

The phenomena that are connected with the surface tension are called capillary phenomena. They include the above mentioned contact angle, as well as the capillary raise or depression of liquids in narrow tubes against gravity forces, capillary waves, etc. Many of these manifestations have been used to experimentally determine the value of γ.

Exercise: consider a cylindrically-shaped liquid body (a water jet from a garden hose for example). Show that the cylinder is unstable against break-up into droplets of dimension of the order of the initial diameter. Hint: assume a

transversal sinusoidal deformation of the wall of wavelength λ and amplitude a. The total surface energy (=integral of γdA) decreases for increasing amplitude a, for the unstable wavelength.

8. Surface forces

In the preceding discussion of the effects of γ, the liquid films or droplets in contact with a solid or liquid surface were supposed to be macroscopic, or more precisely thicker than the range of the interaction forces with the surface. If the liquid film is very thin, then the energy of a molecule is not saturated since no other molecules of the same liquid exist beyond the surface. In other words, the free energy F (per unit surface), of the liquid in the film is different from that in the bulk material. As the film changes thickness, so does F. The thickness (z) variable has a conjugate one, in complete analogy with the pressure and volume where p = -∂F/∂V. So we have a new magnitude Π, for thin films, which is defined by the relation:

$$\Pi = -\partial F/\partial z \qquad (31)$$

Π is called the disjoining pressure, and has the dimensions of force per unit area. Π depends on z (in addition to other thermodynamic variables, such as T, etc.). As the film thickens to macroscopic values, Π obviously goes to zero. The disjoining pressure was introduced by Derjaguin, and is an important parameter to describe wetting phenomena of submicroscopic films.

The surface tension of an interface is a measure of the energy difference between fully coordinated atoms in the bulk and partially coordinated atoms near the surface. The forces of interaction between the atoms have a range that depends on the nature of the forces. For example they can be of very short range, ~1Å in chemical covalent bonds, or of tens or hundreds of Å in electrostatic (ionic) type interactions. Electrostatic forces are rarely manifested by a full Coulombic dependence of the $1/r^2$ form except very close to the ion, because of polarization effects, in particular by other ions or dipoles in the

medium. For example, in ionic solids the field outside the surface decays much faster that $1/r^2$ due to the multipole assembly of lattice ions. In solutions, ions of the opposite charge accumulate in the vicinity of the ions in such a way that the electric field is shielded, as in the Debye model used above.

a. Dipole-dipole interactions

As an example of the interaction between neutral objects lets consider the dipole-dipole interaction. It is simple to show that the interaction energy of two dipoles with dipole moments p_1 and p_2 forming angles θ_1 and θ_2 with the line adjoining them is:

$$E(r,\theta_1,\theta_2,\varphi) = -\frac{p_1 \cdot p_2}{4\pi\varepsilon_o r^3}[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\varphi] \qquad (32)$$

where φ is the angle between the planes through the respective dipoles and connecting line. Dipoles with fixed orientations occur only in crystalline polar molecules. More often, due to thermal agitation the dipoles rotate quasi randomly. The average interaction energy in this case can be found by using Boltzman statistics, where a weight is assigned to each orientation according to the factor exp(-E($\theta_1,\theta_2,\varphi$)/kT). We give here just the result of such averaging.

$$\langle E \rangle = \frac{\int E(\Omega).e^{-E(\Omega)/kT}d\Omega}{\int e^{-E(\Omega)/kT}d\Omega} = -\frac{\partial}{\partial t}\log\int e^{-E(\Omega)/kT}d\Omega$$

where $t \equiv 1/kT$. After integration over the θ's and φ, only the second order term in the expansion of the exponential (which contains $(E/kT)^2$, assuming E << kT), gives a non-zero contribution. The thermally averaged energy (keeping r constant) is:

$$E(r) = -\frac{p_1^2 \cdot p_2^2}{3(4\pi\varepsilon_o)^2 kTr^6} \qquad (33)$$

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This is called the Keesom interaction.

Exercise: calculate the order of magnitude of the Keesom interaction for water molecules.

b. The Van der Waals-London interaction

Another $1/r^6$ type interaction arises between neutral, non-polar atoms or molecules, due to "induced" dipoles, which is a purely quantum mechanical effect. This is the Van der Waals or London interaction. It is simple to deduce an expression for this interaction in the semiclassical picture of the Bohr atom. The electrons are "orbiting" around the nucleus and therefore there is an instantaneous dipole moment p_1 (~Bohr radius x charge). This produces a field E, that decays as $2p_1/r^3$. In turn this field polarizes other atoms and induces in them a dipole $p_2 = \alpha\varepsilon_o E$, α = polarizability. The interaction energy is therefore:

$$E(r) = -\frac{2 p_1 \cdot p_2}{4\pi\varepsilon_o r^3} = -\frac{4\alpha p_1^2}{4\pi\varepsilon_o r^6} \qquad (34)$$

$p_1 = a_o.e$, (Bohr radius times the electron charge).

$\alpha = \dfrac{e^2}{\varepsilon_o m\omega^2}$, which can be related to the ionization energy by the relation:

$\hbar\omega = \dfrac{e^2}{2(4\pi\varepsilon_o).a_o}$; this gives:

$$E(r) = -\frac{\alpha^2\hbar\omega}{\left(4\pi\varepsilon_o\right)^2 r^6} = -\frac{\alpha_1\alpha_2\hbar\omega_1\omega_2}{\left(4\pi\varepsilon_o\right)^2 r^6(\omega_1+\omega_2)} = -\frac{C}{r^6} \qquad (35)$$

The first equality is for a pair of identical atoms, the second is for dissimilar atoms.

Exercise: Calculate the order of magnitude of the forces. Using $\alpha \approx 4\pi\varepsilon_o a_o^3$, one gets C ~ 3.10^4 kT_{RT} $Å^6$. So, for molecular distances of a few angstroms ($3.5^6 = 2\times10^3$), E~ 10kT.

The quantum mechanical origin of E appears only through the use of the Bohr radius and polarizability, which contain Planck's constant h. A more elegant deduction of this interaction that brings the quantum effects in a clear way is given in Kittel's Solid State Physics book. The interaction is the result of the decrease in the zero point energy of the interacting dipoles.

Another remark about the London force is that it assumes infinite propagation speed of the fields of the interacting dipoles. Since the speed of light is the maximum speed, it is clear that at sufficiently large distances ($r >> c/v$) there will be a phase lag of more than 180^0 between the exciting field and reemitted field (photon) as it reaches the source. The effect of this is to decrease the strength of the interaction. This is the so-called retardation effect. Casimir and Polder [Phys. Rev. 73, 36 (1948)] showed that retardation leads to a different distance dependence: $E \sim -C_{ret}/r^7$. So the exponent in the power law increased from 6 to 7 as the distance increases beyond the wavelength of the photons of freq. v.

c. The Lifshitz dielectric theory

When going from isolated atoms and molecules to a solid, the London formula requires modifications. This is because the interaction of many particles is not linear, i.e., the principle of superposition does not apply. In effect, a particle interacting with a third one is already influenced by the first particle and therefore the dipoles are no longer randomly oriented. A complete formulation of the problem must consider the response of the material as a whole. This is done in the dielectric theory of Lifshitz, later also developed by others (Mahanty and Niham, etc.). The interaction, due to fluctuating electromagnetic fields (photon exchange) is calculated using Maxwell equations. Therefore the result includes already the relativistic effects, in particular retardation. The formulas will include the dielectric function $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$, where the imaginary part ε'' is responsible for the dissipation (absorption) of the propagating electromagnetic

field. The Kramers-Kronig relation connect $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$. A corollary of this is the relation:

$$\varepsilon(iv) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \varepsilon''(\omega)}{\omega^2 + v^2} d\omega$$

which tells us that $\varepsilon(i\omega)$ is a real quantity of a pure imaginary argument connected with $\varepsilon''(\omega)$.

The deduction of the Lifshitz formula is rather complicated. We give here the final result. The force between two plane parallel bodies separated by a distance z is:

$$F(z) = -\frac{kT}{\pi c^3} \sum_{n=0}^\infty{}' \int_1^\infty x^2 v_n^3 \left\{ \left[\frac{(s_1 + x)(s_2 + x)}{(s_1 - x)(s_2 - x)} e^{\frac{2xv_n z}{c}} - 1 \right]^{-1} + \left[\frac{(s_1 + \varepsilon_1 x)(s_2 + \varepsilon_2 x)}{(s_1 - \varepsilon_1 x)(s_2 - \varepsilon_2 x)} e^{\frac{2xv_n z}{c}} - 1 \right]^{-1} \right\} dx$$

(36)

The prime in the summation indicates that the first term (n=0) is to be halved ($\times$ ½). $s = \sqrt{\varepsilon - 1 + x^2}$, $\varepsilon = \varepsilon(i\omega)$, and v_n is a multiple of the infrared frequency $(2\pi kT/\hbar)n = 4.10^{13}$ s^{-1}.n (n=1,2,…), at 300K. In the limit of low temperatures or very close distances, Lifshitz showed that the summation can be approximated by an integral ($kT \sum_{n=1}^\infty = \hbar \int_{v1}^\infty dv$). The low temperature limit means z<<hc/kT. At room temperature for example this means z << 50 μm.

Two limits are important. For z << λ, a critical wavelength, the exponentials increase very fast and the formula simplifies to:

$$F(z) = -\frac{\hbar}{8\pi^2 z^3} \int_0^\infty \frac{[\varepsilon_1(iv) - 1][\varepsilon_2(iv) - 1]}{[\varepsilon_1(iv) + 1][\varepsilon_2(iv) + 1]} dv \qquad (37)$$

As we know, the value of $\varepsilon(i\upsilon)$ decreases to 1 as υ increases, and for a certain υ_o, the higher values do not contribute much to the integral. The wavelength λ is then $\sim c/\upsilon_o$. We can see that this produces a z^{-3} law.

The other extreme is large distances $z \gg \lambda$. Now the integration can be again simplified to give a z^{-4} dependence, i.e., retardation. The important values of $\varepsilon(i\upsilon)$ are for $\varepsilon=0$, i.e., the static dielectric constant ε_o. For two identical dielectrics the formula is:

$$F(z) = -\frac{\pi^2 \hbar c}{240 z^4}\left(\frac{\varepsilon_o - 1}{\varepsilon_o + 1}\right)^2 \times \vartheta(\varepsilon_o) \qquad (38)$$

where the last term is of order unity (~ 0.5).

d. Interaction between molecules in a dielectric medium

The interaction between any two molecules 1 and 2, with consideration of the medium in which they are immersed (and therefore becomes polarized too) has been presented in a generalized form by McLachlan. The formula is applicable to permanent dipoles as well (Keesom interaction). The result is:

$$E(r) = -\frac{6kT}{(4\pi\varepsilon_o)^2 . r^6} \times \sum_{n=0}^{\infty}{}' \frac{\alpha_1(i\upsilon_n).\alpha_2(i\upsilon_n)}{\varepsilon_3^2(i\upsilon_n)} \qquad (39)$$

where the symbols have similar meaning as before. $\alpha(i\upsilon_n)$ is the polarizability of the molecules, and ε_3 the dielectric permitivity of the medium.

Lets examine the case of a molecule with a single ionization frequency, ν_I, in vacuum. In that case:

$$\alpha(\upsilon) = \frac{\alpha_o}{1-(\upsilon/\upsilon_I)^2} \quad (40), \quad \text{so that} \quad \alpha(i\upsilon) = \frac{\alpha_o}{1+(\upsilon/\upsilon_I)^2} \qquad (41)$$

Since for most atoms and molecules ν_I is in the ultraviolet (~ 10eV) ~ 5.10^{14} s^{-1}, we see that $\alpha \sim \alpha_0$, in the infrared and visible part. For a rotating dipole, with a characteristic relaxation frequency $\nu_{rot} \sim 10^{11}$ s^{-1}, the polarizability is

$$\alpha(i\upsilon) = \frac{p^2}{kT(1 + (\upsilon/\upsilon_{rot}))} \qquad (42)$$

At zero frequency these two formulas combine into the known Debye-Langevin equation:

$$\alpha(0) = \frac{p^2}{3kT} + \alpha_0$$

If we introduce these expressions in the McLachlan formula we get:

$$E(r)_{v=0} = -\frac{3kT}{(4\pi\varepsilon_o)^2 r^6}[\frac{p_1^2}{3kT} + \alpha_{10}][\frac{p_2^2}{3kT} + \alpha_{20}]$$

for the static or zero frequency contribution.

For $\nu > 0$, we replace the summation by an integral, as before. So,

$$E(r)_{v>0} = -\frac{6\hbar}{(4\pi\varepsilon_o)^2 r^6}\int_{v1}^{\infty}\alpha_1(i\upsilon).\alpha_2(i\upsilon)d\upsilon$$

If we use the simple formula (41) for the polarizability of atoms with one single frequency (ω_1 and ω_2), the integral is very simple and gives:

$$E(r)_{v>0} = \frac{\alpha_{01}\alpha_{02}\hbar\omega_1\omega_2}{(4\pi\varepsilon_o)^2 r^6(\omega_1 + \omega_2)}$$

i.e., the London formula of eqs. (34) and (35). The calculations can be repeated for molecules inside a medium. Instead of using the polarizabilities of isolated molecules, we use the Clausius-Mosotti relation:

$$\alpha_1(\upsilon) = 4\pi\varepsilon_o.\varepsilon_3(\upsilon)\frac{\varepsilon_1(\upsilon)-\varepsilon_3(\upsilon)}{\varepsilon_1(\upsilon)+2\varepsilon_3(\upsilon)}a_1^3 \qquad (43)$$

(a_1 is the atomic radius). We get then:

$$E(r)_{\upsilon=0} = -\frac{3kTa_1^3a_2^3}{r^6}\frac{\varepsilon_1(0)-\varepsilon_3(0)}{\varepsilon_1(0)+2\varepsilon_3(0)}\frac{\varepsilon_2(0)-\varepsilon_3(0)}{\varepsilon_2(0)+2\varepsilon_3(0)} \qquad (44)$$

and

$$E(r)_{\upsilon>0} = -\frac{6\hbar a_1^3a_2^3}{r^6}\int_0^\infty \frac{\varepsilon_1(i\upsilon)-\varepsilon_3(i\upsilon)}{\varepsilon_1(i\upsilon)+2\varepsilon_3(i\upsilon)}\frac{\varepsilon_2(i\upsilon)-\varepsilon_3(i\upsilon)}{\varepsilon_2(i\upsilon)+2\varepsilon_3(i\upsilon)}d\upsilon \qquad (45)$$

This can be integrated for simple cases, like the atom with one single frequency. Since the integration starts at $\upsilon \geq \upsilon_{n=1}$, which is an infrared freq., the dielectric constants can be replaced by their values in the visible. There $\varepsilon = n^2$, where n is the refractive index. The integration gives, in the even simpler case where all three freqs. (mol. 1 and 2, and medium 3) are the same (= υ_0),

$$E(r) = E_{\upsilon=0} + E_{\upsilon>0} \approx -\frac{3kTa_1^6}{r^6}\left(\frac{\varepsilon_1(0)-\varepsilon_3(0)}{\varepsilon_1(0)+2\varepsilon_3(0)}\right)^2 - \frac{3^{1/2}h\upsilon_0a_1^3}{4r^6}\frac{(n_1^2-n_3^2)^2}{(n_1^2+2n_3^2)^{3/2}} \qquad (46)$$

Because usually $kT << h\upsilon_0$, the second term dominates. Another interesting point is that it shows that in a medium, the Van der Waals force between molecules can be both attractive, if $n_1 > n_3$, or repulsive, if $n_1 < n_3$. This is because the medium polarizes in such a way that the mediated interaction is repulsive. In other words, the attraction between molecules 1 and 2 is less that the attraction between the molecules and the medium. This is similar to the image charge being of the same sign (leading to self-repulsion) if the object

charge is inside a dielectrically dense medium. We will retake this subject in the next section.

9. The Hamaker constant

In this section we will use a much simpler model to illustrate the origin and effect of unsaturated forces on the atoms near the surface. We will assume that particles interact with each other with $-1/r^6$ forces and that these forces are additive, an assumption which we know is not correct. In spite of this, the procedure gives surprisingly good results. We want in particularly to analyze the effect of finite film thickness on its interaction with the surface. The geometry of our problem is shown in the figure. The total energy of a molecule inside medium 1 is:
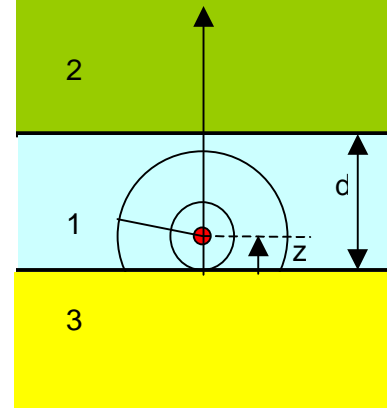
$$E(r) := -A_{11} \cdot n_1 \cdot \int_a^z \frac{4 \cdot \pi \cdot r^2}{r^6} dr - A_{11} \cdot n_1 \cdot \int_z^{d-z} \frac{2 \cdot \pi \cdot r \cdot (z+r)}{r^6} dr - A_{11} \cdot n_1 \cdot \int_{d-z}^{\infty} \frac{2 \cdot \pi \cdot r \cdot d}{r^6} dr \dots$$

$$- A_{13} \cdot n_3 \cdot \int_z^{\infty} \frac{2 \cdot \pi \cdot r \cdot (r-z)}{r^6} dr - A_{12} \cdot n_2 \cdot \int_{d-z}^{\infty} \frac{2 \cdot \pi \cdot r \cdot (r-d+z)}{r^6} dr \tag{47}$$

where the first three terms represent the energy due to similar molecules in the film. The integration starts at r = a, the diameter of a molecule. The A's are the constants in the van der Waals attractive energy terms. The n's are the particle densities. We use the well-known geometrical formula of the area of a sector between two parallels in the surface of a sphere:
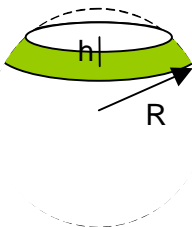
Area of shaded sector = $2\pi Rh$ (48)

The result of the integration is:

$$E_1 = -\frac{4\cdot\pi\cdot n_1\cdot A_{11}}{3\cdot a^3} + \frac{\pi\cdot n_1\cdot A_{11}}{6\cdot z^3} + \frac{\pi\cdot n_1\cdot A_{11}}{6\cdot(d-z)^3} - \frac{\pi\cdot n_3\cdot A_{13}}{6\cdot z^3} - \frac{\pi\cdot n_2\cdot A_{12}}{6\cdot(d-z)^3} = E_{11} + E_{12} + E_{13}$$

$$(49)$$

For z $\rightarrow\infty$, $E_1 = -\dfrac{4\pi n_1 A_{11}}{3a^3}$ which should be the bulk cohesive energy per molecule of medium 1. For z > d, similar expressions are obtained:

$$E_2 = -\frac{4\pi n_2 A_{22}}{3a^3} + \frac{\pi n_2 A_{22}}{6(z-d)^3} + \frac{\pi n_1 A_{12}}{6z^3} - \frac{\pi n_1 A_{12}}{6(z-d)^3} - \frac{\pi n_3 A_{23}}{6z^3} \qquad (50)$$

and, for z<0:

$$E_3 = -\frac{4\pi n_3 A_{33}}{3a^3} - \frac{\pi n_3 A_{33}}{6(z-d)^3} + \frac{\pi n_1 A_{13}}{6z^3} - \frac{\pi n_1 A_{13}}{6(z-d)^3} + \frac{\pi n_2 A_{32}}{6(z-d)^3} \qquad (51)$$

To calculate the total energy of the system, we must integrate these expressions. One obtains:

$$2E_{total} = \int_{-l}^{0} E_3.S.dz + \int_{0}^{d} E_1.S.dz + \int_{d}^{l} E_2.S.dz = 2(E_{tot1} + E_{tot2} + E_{tot3}) \quad (52)$$

The factor 2 is to account for the double counting of pairs. The integral limits are not 0 and d, but should exclude the molecular radius (a/2) and d-a/2. *L* is a large distance. The result is:

$$E_{tot1} = -e_1.V_1 + (\gamma_{12} + \gamma_{13}).S - \frac{H_1}{12.d^2}\cdot S \qquad (53)$$

The constants are: $e_1 = \dfrac{4\pi n_1^2 A_{11}}{3a_1^3}$ (energy per unit volume)

$$\gamma_{12} = \frac{\pi n_1}{3a_1^2}(n_1 A_{11} - n_2 A_{12}) \qquad (54)$$

and $\quad \gamma_{13} = \dfrac{\pi n_1}{3a_1^2}(n_1 A_{11} - n_3 A_{13}) \qquad (55)$

$$H_1 = \pi n_1 [(n_1 A_{11} - n_2 A_{12}) + (n_1 A_{11} - n_3 A_{13})] \quad (56)$$

The other two integrals give:

$$E_{tot3} = -e_3 V_3 + \gamma_{31}.S + \frac{H_3}{12.d^2} \cdot S \qquad (57)$$

the constants have similar meanings: e_3 = energy per u. vol. In medium 3.

$$\gamma_{31} = \frac{\pi n_3}{3a_3^2}(n_3 A_{33} - n_1 A_{13}) \qquad (58)$$

and
$$H_3 = -\pi n_3 (n_1 A_{13} - n_2 A_{23}) \qquad (59)$$

Similarly,

$$E_{tot2} = -e_2 V_2 + \gamma_{21}.S + \frac{H_2}{12.d^2} \cdot S \qquad (60)$$

$$\gamma_{21} = \frac{\pi n_2}{3a_2^2}(n_2 A_{22} - n_1 A_{12}) \qquad (61)$$

and
$$H_2 = -\pi n_2 (n_1 A_{12} - n_3 A_{23}) \qquad (62)$$

Finally:

$$E_{total} = -E_{vol} + \tilde{\gamma}_{12}.S + \tilde{\gamma}_{13}.S - \frac{A}{12\pi d^2} \qquad (63)$$

Where: $\tilde{\gamma}_{12} = \gamma_{12} + \gamma_{21}$ and $\tilde{\gamma}_{13} = \gamma_{13} + \gamma_{31}$ (64)

The so-called Hamaker constant A is:

$$A = \pi^2 (n_1^2 A_{11} - n_1 n_2 A_{12} - n_1 n_3 A_{13} + n_2 n_3 A_{23}) \qquad (65)$$

It can be shown that: $A_{12} \approx \sqrt{A_{11} A_{22}}$, and similarly for A_{13}. The quantity: $v_1 = n_1 \sqrt{A_{11}}$, is related to the index of refraction of medium 1, $v^2 = n^2 A$ ~refrac. Index, see last section. There we used the letter n for the index of refraction.

$$A \cong \pi^2 (v_1 - v_2).(v_1 - v_3) \qquad\qquad (66)$$

Special cases:

a) $n_1 = n_3 = 0$. This is the simple case of a free surface. The energy is simply:

$$E = - e.V + \gamma S \qquad \text{(we dropped the indices)}$$

We see the meaning of the parameters:

$$e = \frac{4\pi n^2 A}{3a^3}, \qquad\qquad \gamma = \frac{\pi n^2.A}{6a^2} = \frac{\pi v^2}{6a^2} \qquad\qquad (67)$$

b) $n_1 = 0$. Two media (2 & 3) separated by vacuum.

$$E = E_{vol} + \gamma_2 S + \gamma_3 S - \frac{\pi^2 n_2 n_3 A_{23}}{12\pi d^2}, \qquad\qquad (68)$$

which is always an attractive force.

Exercise: Orders of magnitude: A_{23} is of order ~10^{-77} Jm^6, and the densities are n ~ 10^{28} m^{-3}. Therefore, the Hamaker constant is A ~ 10^{-19} J ~0.1-1 eV ~4-40 kT.

c) Thin film on a surface ($n_3 \approx 0$, vapor; solid, $s = 2$, liquid, $l = 1$):

$$E = E_{vol} + \gamma_{sl} S + \gamma S - \frac{A}{12\pi d^2} \qquad\qquad (69)$$

The gamma's are the solid-liquid and vapor-liquid surface tensions.

$$A = \pi^2 (n_1^2 A_{11} - n_1 n_2 A_{12}) \cong \pi^2 v_l (v_l - v_2) \qquad (70)$$

We have the following interesting result that if $\nu_1 > \nu_2$, i.e., if the liquid is optically denser than the solid, there is attraction between the surfaces. This means that the film is unstable against collapse (droplet formation) that brings the surfaces together in parts of the film, and of course far away in others to keep the volume constant. If on the contrary $\nu_1 < \nu_2$, the film is stable since the two surfaces repel each other. The film wets the solid surface. If one considers a solid covered by a liquid film of the same substance (like in melting), usually $\nu_l < \nu_s$, so that the melt wets its solid. In the case where $\nu_l > \nu_s$, the liquid does not wet its own solid. However this result is not applicable to water, since the interactions are not properly described by a Van der Waals formula.

An interesting case is that where there is no forces between surfaces. This is convenient in AFM applications. A dielectric fluid with this property will suppress the van der Waals forces between tip and surface. The condition $A = 0$, is fulfilled for $\nu_1 = \nu_2$, or $\nu_1 = \nu_3$. For ν_1 in between these two values, there is repulsion between tip and surface. For ν_1 outside the two values, there will be attraction.

10. Microscopic wetting theories

We are now ready to re-examine the wetting of liquids on solid surfaces which we described above (section 7) for the macroscopic case where surfaces and interfaces were characterized by their tensions (γ) alone. The macroscopic approach means that the size of the liquid film (thickness) or droplets (height), is larger than the range of the surface forces (up to ~ 1000 Å). Below that, the energy per molecule is not saturated to its bulk value, and if we use the bulk surface or interface tensions, we must correct for the surface forces.

Surface forces give rise to the concept of disjoining pressure. We have seen forces originating from Van der Waals interactions that decay as $1/r^6$. We have seen that since there are three media involved, the disjoining pressure can be attractive or repulsive, depending on the value of the dielectric constants. Other forces besides Van der Waals can also be present, for example chemical and structural forces due to the short range interaction between molecules and

between molecules and the substrate, electrostatic forces, "double layer" forces from solvated ions, hydrophobic and hydrophilic forces due to H-bonds, etc. A good discussion of the various surface forces can be found in the book of J. Israelachvili.

Sufficiently far away from the surface, when most stronger forces have already decayed, the Van der Waals force always remains. As we have seen, the potential energy is of the form:

$$P(z) = \frac{A}{12\pi z^2},$$
(66)

$$A = A_{sl} - A_{ll}$$
(67)

The disjoining pressure in this case is:

$$\Pi(z) = \frac{A}{6\pi z^3}$$
(68)

which can be attractive or repulsive. The free energy of a surface covered by a thin film is then:

$$G(z) = \gamma_{sl} + \gamma + P(z),$$
(69)

P(z) is a decreasing function of z (in absolute value). In the limit when z→0 we must have *G(0) = γ_sv* , which is the solid-vapor surface tension. Therefore the limiting value of *P(z→0) = S = γ_sv - γ_sl - γ* , which is the spreading coefficient.

If the solid surface is exposed to a vapor that condenses on its surface, a term equal to $(\mu_l - \mu_v).z / v_{mol}$, must be added to G(z). If $\mu_l < \mu_v$ the liquid will always condense and form a thick film. If $\mu_l > \mu_v$, a thin film might still form provided that P>0.

The shape of a thin liquid film on a surface depends on the sign of the two important magnitudes S and P. We have seen that if P>0, the liquid-vapor and the solid-liquid interfaces "repel" each other or the disjoining pressure is positive (we have to press against the liquid surface to keep it from expanding). If S>0, the film wants to spread. These two opposing tendencies equilibrate by the

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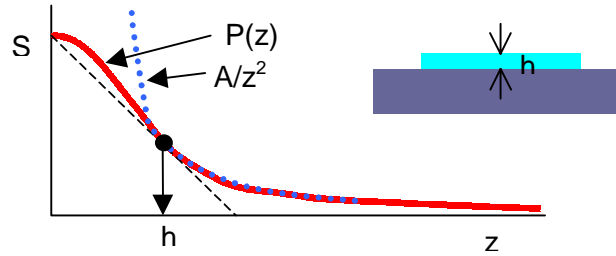
formation of a flat pancake of thickness, h. The value of h can be found by minimization of G at constant liquid volume V:

$$G(z) = G_0 - A.S + A.P(z), \qquad (70)$$

With $V = A.z =$ constant. Minimization gives:

$$S = h.\Pi(h) + P(h) \qquad (71)$$

It is easy to see how to determine h graphically: it is determined from the tangent of a line through (z=0, S) to the $P(z)$ curve:

The profile of the pancake near its edge can be found by minimization of G(z) subject to the constraint of constant volume (as will be done below). The result is a parabolic shape: $z^2 = 2a(x-x_L)$.

In the case where S<0 and P<0 (A<0), droplets will form with a shape that can be determined by minimization of:

$$G = G_0 + \int_{drop} 2\pi r dr \left\{ -S + \frac{\gamma}{2}\left[\frac{dz}{dr}\right]^2 + P(z) - \frac{\mu_{vapor} - \mu_{liq}}{v_{mol}}.z \right\} \qquad (72)$$

subject to the condition that: $V = \int_{drop} 2\pi r[z]dr$, is constant. We assumed circular droplets with very shallow contact angle. The last term in the expression applies in the case where the droplet is growing in size due to condensation. We will assume no growth, i.e., $\mu_{vapor} = \mu_{liquid}$. The solution of (72) by the method of Lagrange multipliers requires numerical methods in general. However, in the

special case where the droplet shape is very close to a spherical cap, a situation that is observed in many experimental situations, the following solution for the contact angle ($\varphi \equiv 2h/r$) is found:

$$\varphi^2 = \varphi_0^2 + \frac{2}{\gamma}.[P(h) + h.\Pi(h)] \qquad (73)$$

where φ is the contact angle of the droplet of height h and φ_0 = macroscopic contact angle. This simple formula predicts that the contact angle decreases as h decreases (P, Π<0). This is to be expected since in this case the surface of the liquid and the solid "attract" each other, which tends to flatten the drop.

Other interesting cases of wetting occur depending on the signs of S and P, and its shape. One interesting case is where A<0 and S>0. In this case G(z)
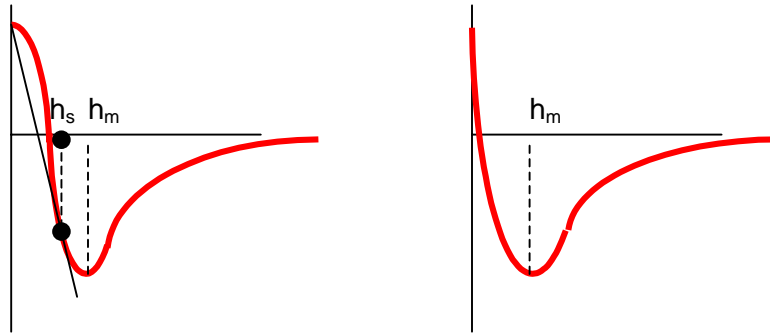
must have a minimum at a certain thickness h_m.

If the figure on the left applies, first a flat droplet (pancake) will form with height h_s, if the liquid volume is small enough. This is a stable minimum since the curvature of the potential is positive a this point. Once this thin pancake covers the surface completely, a discontinuity will occur and a film of thickness h_m will form. Its thickness will remain constant at h_m and any excess liquid will form a droplet on top. This is called pseudo partial wetting.

If the case of the right figure applies, then, a two-dimensional gas will form first and then a pancake of thickness h_m. After this, droplets will form again on top of the film. The contact angle of the droplet on top of its own film is given by $\gamma_m = \gamma\cos\varphi$, where $\gamma_m = \gamma + h_m\Pi(h_m)+P(h_m)$. The shape of the foot of the droplet is now hyperbolic.

Another situation is given when the following potential function applies:
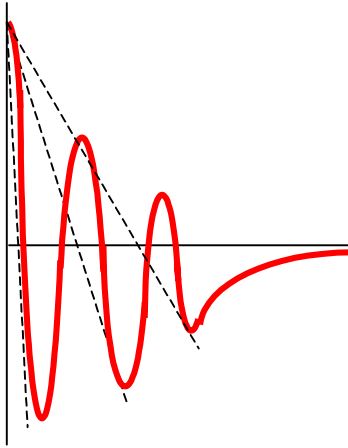
The oscillatory nature of P(z) is due to the short range forces: chemical, and structural. The minima are spaced by the molecular thickness. Stable minima are found at positions corresponding to layer-by-layer growth.

These and other situations are discussed in detail in various papers by P. De Gennes and collaborators. Another discussion on this topic can be found in volume 5 of Landau.

One topic of active research today is the structure and properties of the first few molecular layers of liquids near solid walls. For example water near surfaces both inorganic and biological (membranes, proteins), liquid crystals, etc. We will come back to this subject later on, in the chapter on scanning probe microscopies.

11. Equilibrium shape of crystals: Wulf's theorem

Unlike in the liquid materials we have been studying till now, the surface tension of crystalline solid materials, depend on the atomic arrangement at the surface, which depends on the orientation, i.e., on the surface Miller indices. For that reason the equilibrium shape of a crystal as it solidifies from a liquid drop, changes from spherical to polyhedral. Intuitively one expects low surface tension orientations to be predominant. This will undoubtedly include the most compact surfaces, i.e., with low Miller index, since there the number of broken bonds is

minimal. The first treatment of the problem was by Wulff in 1901. Here is his theorem:
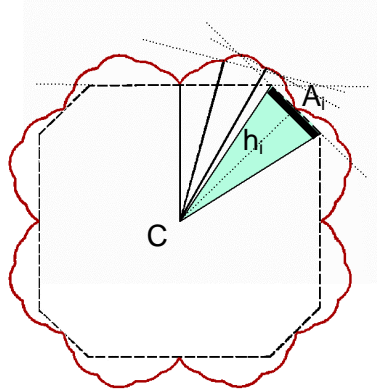
Consider a crystal polyhedron (broken lines in the figure) delimited by surfaces A_i, in equilibrium with its vapor. These surfaces are at a distance h_l from the center C. Large surfaces are closer to the center than smaller ones, as shown in the figure.

In equilibrium we must have: $\delta\Omega = -p_s\delta V_s - p_v\delta V_v + \Sigma_i \, \gamma_i \, \delta A_i = 0$

The conditions are: total volume constant: $V = V_s + V_v$

same chemical potential: $\mu_s = \mu_v$

uniform temperature: $T = \text{constant}$

The crystal volume is: $V_s = \Sigma_l \, \frac{1}{3} A_l h_l$, so that $\delta V_s = \frac{1}{3}\Sigma_i \, [h_i \, \delta A_i + A_i \, \delta h_i]$

From the figure we see also that $\delta V_{s,i} = A_i \, \delta h_i = \frac{1}{3}(h_i \, \delta A_i + A_i \, \delta h_i) = \frac{1}{2}(h_i \, \delta A_i)$.

Substituting into $\delta\Omega$, with $\delta V_s = -\delta V_v$, we get finally

$$\Sigma_i \, \{\frac{1}{2}(-p_s + p_v)h_i + \gamma_i) \, \delta A_i = 0$$

This should be true for any value of δA_i (they are independent variables). Therefore,

$$\gamma_i \, / \, h_i = \text{constant} \qquad\qquad (74)$$

This is Wulff's theorem. It implies that the areas of the facets exposed by the crystal can be obtained by tracing radii in the appropriate direction with a length proportional to γ_i and a plane perpendicular to the radius vector. The minimal polyhedron delimited by the intersection of the innermost planes is the equilibrium shape.

Although the construction in the previous figure shows flat surfaces delimiting the crystal polyhedron, it is not obvious that the flat facet under a sharp cusp (a low Miller index plane) should be delimited by other flat facets, as indicated in the drawing. In fact the envelope of tangents can be curved:
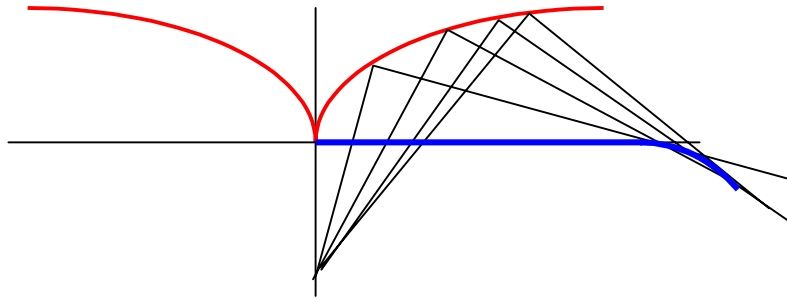
The shape of $\gamma(\mathbf{n})$ changes from spherical, when the crystal is liquid (melted) to one with cusps at the positions of the most stable surfaces, which are the low Miller index planes. There, the atoms lose the least amount of bonds by the truncation of the crystal. For example, in an fcc or hcp crystal, the coordination goes from 12 in the bulk to 9 in the (111) surface, and to 8 in the (100) surfaces. The formation of singularities or cusps is due to the discrete nature of matter, so that when the orientation changes steps are formed. The interaction between steps determines the nature of the cusp, as we shall see next.

12. Stability of crystal surfaces: faceting

Wulff's theorem applies to the equilibrium shape of a crystal, which means that the kinetic processes of atomic rearrangements are sufficiently fast. This applies to small crystallites. A large crystal maybe prepared with a surface not in the Wulff construction, and yet be kinetically frozen. So, now we want to

examine the stability of surfaces towards small deviations of structure. In particular faceting, where a planar surface decomposes into a hill and valley structure with the same average orientation:

The sides of the hills should be orientations of higher stability. The following treatment, due to N. Cabrera (1962), considers this problem as one similar to the equilibrium between bulk phases, the phases here being the new facets.

The change of free energy for a volume-conserving transformation where the surface A changes into A' is:
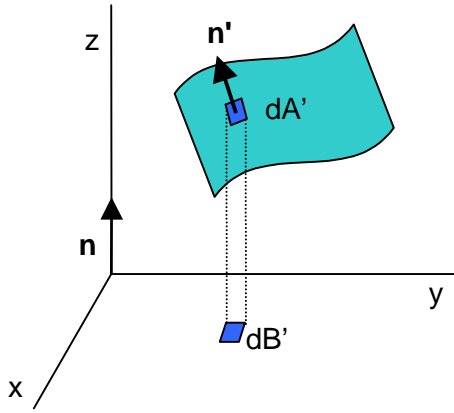
$$\Delta \Omega = \int_{A'} \gamma(\vec{n}') dA' - \gamma(\vec{n}) . A \qquad (75)$$

The new surface A' is described by z = z(x,y) The vector gradient is perpendicular to it its components are $(-\frac{\partial z}{\partial x}, -\frac{\partial z}{\partial y}, 1) = $ (p, q, 1); p and q are the tangents of the angles. We define also the vector **p** in the xy plane with components (p,q,0). We have therefore,

$$\vec{n}' \sqrt{1 + p^2 + q^2} = \vec{n} + \vec{p}$$

Where **n'** and **n** are the unit vectors perpendicular to A' and A respectively. The projected area dB' is:

$$dB' = dA'.\cos\theta = \frac{dA'}{\sqrt{1 + p^2 + q^2}} \qquad (76)$$

We will work with projected areas and define the surface tension *per unit projected area* β. The relation between γ and β is simply:

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$$\beta(\vec{p}) = \gamma(\vec{p}).\sqrt{1 + p^2 + q^2}$$

So, instead of (75) we write:

$$\Delta\Omega = \int_{A'} \beta(\vec{p}')dB' - \beta(\vec{p}).B \qquad (78)$$

Before proceeding, lets consider the shape of γ(**p**) or β(**p**). The most stable surfaces are the compact, low Miller index planes, since there the number of broken bonds is minimum. Small deviations from these are called vicinal surfaces. They consist of terraces of the low Miller index plane, separated by steps, usually one atom high. The angle $\theta \approx \tan\theta = p$ (for small values) is equal to *a/L*, where a=step height ($\sim$ 2 Å) and L = terrace width. The number of steps per unit area is 1/L. For small θ, the steps are far away from each other and do not interact and the energy is a linear function of the step density. The energy per unit area is:

$$\beta(\vec{p}) \approx \beta_0 + J.|\vec{p}| + ... > \beta_0 \qquad (79)$$

where *J* is the energy per unit step length (which depends on **p**). The important thing is that (79) expresses the fact that around low Miller index surfaces, the function $\beta(p,q)$ has a conical cusp singularity. Such stable surfaces are called singular surfaces. They include the (111) and (100) planes of fcc materials, the (110) of bcc and the basal, or (0001) planes of hcp. The function $\beta(p,q)$ looks something like the graph:
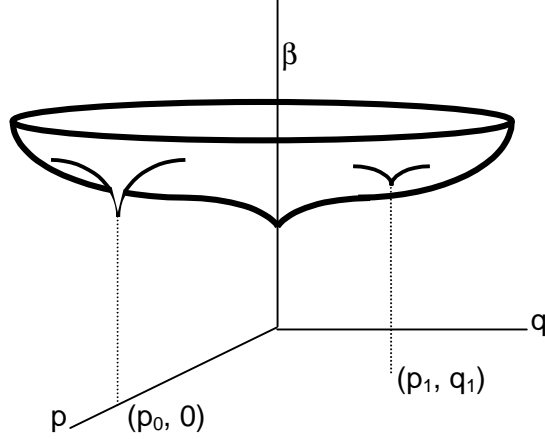
Three cusps have been drawn for three hypothetical singular surfaces. Outside the singularity, $\beta(p,q)$ can be expanded:

$$\beta(\vec{p}') = \beta(\vec{p}) + \frac{\partial \beta}{\partial \vec{p}} \cdot \delta \vec{p} + \frac{1}{2} \delta \tilde{p} \left[\frac{\partial^2 \beta}{\partial \vec{p}^2} \right] \delta \tilde{p} + ... \qquad (80)$$

The third term in (80) is a quadratic form of second order. It can be diagonalized by a transformation of the axis along its eigenvectors:

$$\begin{pmatrix} \dfrac{\partial^2 \beta}{\partial p^2} & \dfrac{\partial^2 \beta}{\partial p \partial q} \\ \dfrac{\partial^2 \beta}{\partial p \partial q} & \dfrac{\partial^2 \beta}{\partial q^2} \end{pmatrix} \rightarrow \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

The eigenvectors point in the direction of the principal axis (principal curvatures) and the eigenvalues are the local curvatures λ_1 and λ_2. With this transformation of coordinates, (80) becomes:

$$\beta(\vec{p}') = \beta(\vec{p}) + \frac{\partial \beta}{\partial \vec{p}} \cdot \delta \vec{p} + \frac{1}{2} \left[\lambda_1 (\delta p_1)^2 + \lambda_2 (\delta p_2)^2 \right] + ... \qquad (81)$$

Upon substitution into (78) the first term in (80) cancels and the integration of the second term is zero because of conservation of the average orientation:
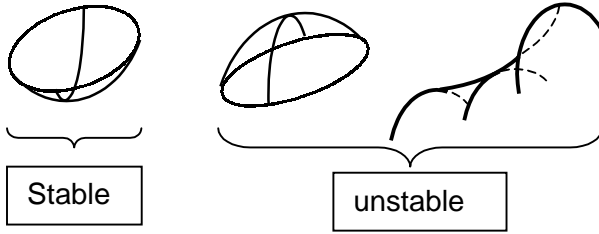
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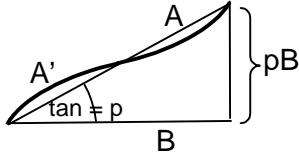
$$\int_B dB' = B \qquad \text{and} \qquad \int_B \delta p'\, dB' = pB$$

So, finally we obtain:

$$\Delta\Omega = \frac{1}{2}\left[\lambda_1 \int_B (\delta p_1)^2\, dB + \lambda_2 \int_B (\delta p_2)^2\, dB \right] \qquad (82)$$

This tells us that if the curvatures are positive ($\lambda_1 > 0$, $\lambda_2 > 0$) the surface is stable, since any change leads to an increase in Ω. If either $\lambda_1$ or λ_2 is negative, the new orientation is unstable. This means that such a surface will decompose into two or more stable surfaces. This situation is akin to an unstable volume phase that will break up into two or three

phases. Each one of these phases must by itself be stable to break-up into a hill and valley structure, so that the principal curvatures of β should be positive. Lets examine a few cases:

a) Coexistence of a singular facet with a non-singular facet. We take origin in the singular facet ($p=q=0$), and we chose the p axis along the new orientation (p_1, 0). The conditions of conservation of projected area and of same initial and final contour (see figure) are:

$$B_1 = B_1' + B_2', \text{ and } B_1 p_1 = B_1' p_1' \qquad (83)$$

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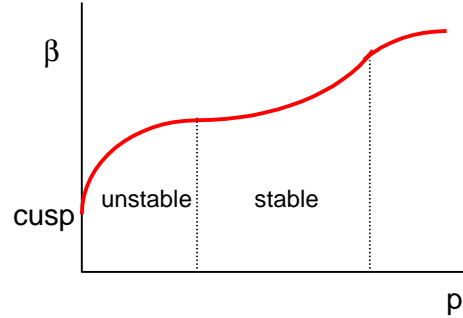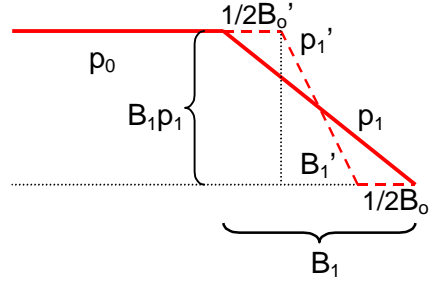
Therefore $\quad \Delta\Omega = \beta(0).B_0' + \beta(p_1').B_1' - \beta(p_1).B_1$, $\qquad$ where $p_1' = p_1 + \delta p_1$

Expanding in series: $\qquad \beta(p_1') = \beta(p_1) + \dfrac{\partial\beta}{\partial p_1}.\delta p_1 + \dfrac{1}{2}\dfrac{\partial^2\beta}{\partial p_1^2}.(\delta p_1)^2 + ...$ $\qquad$ (84)

Substituting and regrouping we find:

$$\Delta\Omega = B_1\left[\frac{\partial\beta}{\partial p_1} - \frac{\beta(p_1) - \beta(0)}{p_1}\right].\delta p_1 + \frac{1}{2}B_1\left[\frac{\partial^2\beta}{\partial p_1^2} - \frac{2}{p_1}\{\frac{\partial\beta}{\partial p_1} - \frac{\beta(p_1) - \beta(0)}{p_1}\}\right].\delta p_1^2 \qquad (85)$$

The stability conditions are: $\delta\Omega = 0$, and $\delta^2\Omega > 0$. The first is satisfied if:
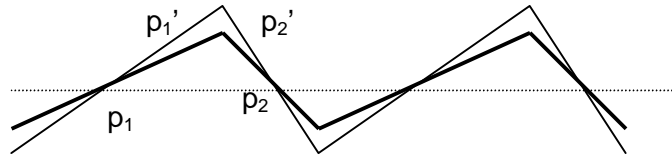
$$\frac{\partial\beta}{\partial p_1} = \frac{\beta(p_1) - \beta(0)}{p_1} \qquad (86)$$

The second is satisfied automatically because we assumed positive curvature.
Equation (86) indicates that the slope of β at point p_1 must be the same as that of
the straight line passing through p_0 and p_1. Graphically this means:

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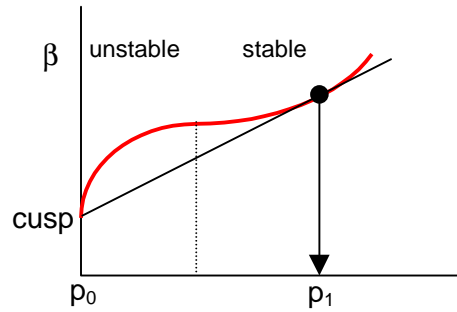
b) Coexistence of two non-singular facets. Again, the two facets must be stable on their own (positive curvature of β).

Similar boundary conditions as before apply:

Conservation of projected area: $B_1 + B_2 = B_1' + B_2'$,

and contour: $B_1 p_1 + B_2 p_2 = B_1' p_1' + B_2' p_2'$

One proceeds in a similar way as before: expand $\beta(p_1')$ and $\beta(p_2')$ around p_1 and p_2, use the boundary conditions to eliminate the B' and one gets a lengthy expression for $\Delta\Omega$ with linear and quadratic terms in the δp's. These linear terms must be zero in equilibrium. In this manner one gets:

$$\frac{\partial \beta}{\partial p_1} = \frac{\beta(p_2) - \beta(p_1)}{p_2 - p_1} = \frac{\partial \beta}{\partial p_2} \qquad (87)$$

which expresses the geometrical condition that the tangents to β at p_1 and p_2,
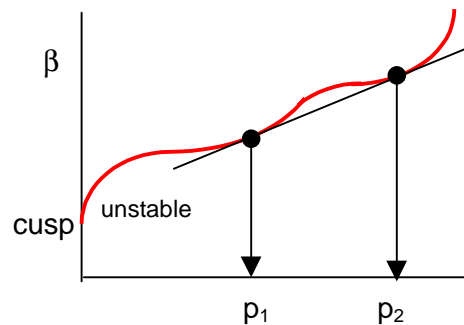
must coincide with the line joining these points.

We thus see that in both of the two cases discussed, the facets resulting from the break-up of an unstable orientation can be obtained by imagining a plane tangent to the β(p,q) surface from below. Since only three points are

needed to define a plane, we arrive at the interesting conclusion that only three facets can be produced upon faceting of an unstable surface.

Free energy or potential of a faceted structure

After an unstable orientation p with projected area B has given rise to facets p_1 and p_2, with projected area B_1 and B_2, the potential of the new structure can be easily obtained from the boundary conditions:

$$B = B_1 + B_2 \quad \text{and} \quad Bp = B_1 p_1 + B_2 p_2$$

$$\Omega = B_1 \beta(p_1) + B_2 \beta(p_2) = B\left[\frac{p_2 - p}{p_2 - p_1} \beta(p_1) + \frac{p - p_1}{p_2 - p_1} \beta(p_2) \right] \qquad (88)$$

which is the equation of the line joining the facets. This line (or plane) goes under the curve β in the unstable areas. The amount or area of each facet follows the lever rule as in the case of phases in equilibrium.

13. The roughening transition

The ad-atom-vacancy Jackson model

In addition to faceting, the break-up of an unstable surface into a hill-and-valley structure of stable facets, other surface modifications take place, even on the stable surfaces. One of these is the roughening transition. Roughening means the formation of vacancies and ad-atoms, steps etc. on an initially flat surface as a result of increases in temperature. The formation of such defects costs energy since bonds must be broken an coordination is lost on average. This increase in energy of the system is counteracted by an increase of entropy due to disorder. At sufficiently high temperature, the free energy may in fact decrease. At this point the surface becomes rough and this defines the roughening transition. To treat the problem theoretically one must know the hamiltonian, i.e., one must have a model for the energy. The situation is not simple due to the many types of disorder one must consider. In practice many

treatments are based on the use of numerical simulation methods, like the Monte Carlo method. Here we present two simple models to capture the essential physics of the problem. Jackson used a mean field approximation in the so-called solid-on-solid model (SOS). In the SOS model the solid consists of lattice of cells containing the atoms (like blocks). The cells can be occupied or empty. The interface with the vacuum is said to be sharp if above it only a few cells are occupied (ad-atoms). It is also sharp if only a few vacancies are present. This is the case at low temperatures. However at sufficiently high temperature, many surface cells are empty and the position of the surface is unclear. Lets say that N_s cells of the surface are occupied and $1-N_s$ are empty. If z_s represents the coordination number and J the energy to break a bond, then the energy E of the system is: number of sites (N_s) x probability that a neighboring site is empty ($1-N/N_s$)z_s x J
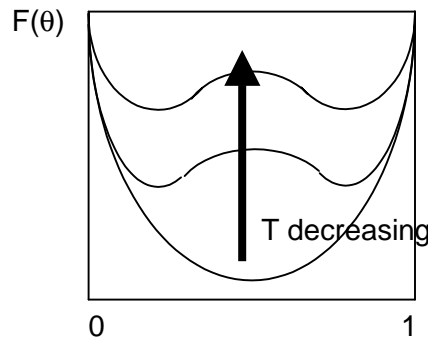
$$E = Jz_s(1-N_s/N)N_s \qquad (89)$$

The entropy S is the logarithm of the number of configurations $W = N!/N_s!(N-N_s)!$ Using Sterling's approximation for the factorial of large numbers:

$$S = k\ln W \approx k[N\ln N - N_s\ln N_s - (N-N_s)\ln(N-N_s)]$$

The free energy is: F = E-TS. Introducing the coverage $\theta = N_s/N$, one obtains:

$$F(\theta) = Jz N\theta(1-\theta) + kTN\{\theta\ln\theta + (1-\theta)\ln(1-\theta)\} \qquad (90)$$

The graph of $F(\theta)$ looks like:

At low temperature F has two minima, one close to $\theta = 0$ and the other close to $\theta = 1$. The surface is well defined, with either a few ad-atoms, or a few vacancies. As the temperature increases the minima move closer to the center and, at the roughening transition T_R, only one minimum exist at the center, i.e., at $\theta = 0.5$. The surface is now undefined (rough). The value of T_R can be found easily by differentiation. One gets:

$$T_R = zJ/2k \qquad (91)$$

Jackson defined a parameter $\alpha = T_R/T_M$, where T_M is the melting temperature. If $\alpha < 1$ the surface roughens before melting, if $\alpha > 1$, it never roughens. The Jackson model is equivalent to then Ising modle of ferromagnetism. The thermodynamics of the Ising system is well known. The specific heat for example shows a logarithmic divergence at T_R. The model however is too simple, since the surface site occupation is always either 0 or 1, and on the surface is always flat. A really rough surface should not remain flat, and the heights of distant points should be uncorrelated such that a divergence sets in.

The step model

Another interesting model of surface roughening is in terms of generation of steps. The surface is modeled by the so-called terrace-step-kink model (TSK). In the mean field approximation, lets consider a step of perimeter L forming a loop on the surface. If J is the energy of an atom at the step, the energy is JL/a, where a is the length of an atom at the step. The entropy of the step can be approximately found as follows. It z_s are the number of possible step orientations (= coordination number), the first one atom segment of the step can take z_s possible orientations, the second z_s-1 since it is not allowed to go back on itself, the third has also z_s-1 possibilities. For L/a atoms of the step the total number of possibilities is $(z_s-1)^{L/a}$, and the entropy is $S = k\ln(z_s-1)^{L/a} = kL/a\ln(z_s-1)$. The free energy is then:

$$F(L) = [J-kT\ln((z_s-1)]L/a \qquad\qquad (92)$$

The roughening transition is:

$$T_R = J/k\ln((z_s-1) \qquad\qquad (93)$$

If $T < T_R$ the free energy is positive and therefore is minimized for $L = 0$. For $T > T_R$ the $F(L)$ decreases when $L\rightarrow\infty$, i.e., the surface roughens.

A better treatment is to consider the roughening of a step as a result of the thermal production of kinks that deform its shape. Lets say that an originally straight step becomes rough, as shown in the figure:
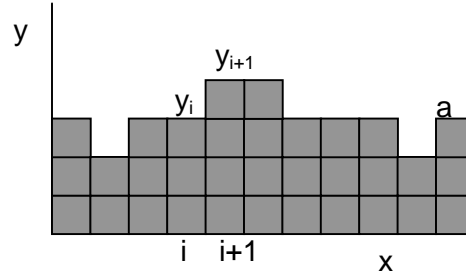
And lets J_x and J_y denote the energy to break a bond in the x and y directions respectively. The total energy for a step of length L is therefore:

$$E = J_y \frac{L}{a} + J_x \sum_{i=1}^{L/a} \frac{|y(i) - y(i-1)|}{a} \qquad\qquad (94)$$

The number $[y(i)-y(i-1)]/a$ can take the values -1, 0, and 1. Therefore the partition function Z is:

$$Z = \left[\sum_{n=-1}^{1} \exp(-\frac{J_y + J_x|n|}{kT}) \right]^{L/a} = e^{-\frac{LJ_y}{akT}} \left[1 + 2e^{-\frac{J_x}{kT}} \right]^{L/a} \qquad\qquad (95)$$

and the free energy per unit step length is:

$$\sigma = -\frac{kT \ln Z}{L} = \frac{1}{a}\left(J_y - kT \ln\left[1 + 2e^{-\frac{J_x}{kT}}\right]\right) \qquad (96)$$

The probability of having a kink at any site is:

$$\langle |n| \rangle = \frac{2e^{-\frac{J_x}{kT}}}{1 + 2e^{-\frac{J_x}{kT}}} \qquad (97)$$

If J_x and J_y were the same, then the roughening transition occurs at the temperature where the free energy of a step becomes zero: $T_R = J/k\ln2$. This is of the same type as the previous ones (see eqs. 91 and 93).

All these previous simple models are within the mean field approximation. Fluctuations are not considered. However, in order to understand the roughening transition correctly fluctuations must be considered. There are several methods to do this, including the variational method and the renormalization group theory method. The treatment is rather involved and we will not be pursued here. Only the result will be stated:

The surface is described (in the SOS model) by the height at each surface cell $h(\mathbf{r})$. Below the roughening transition temperature T_R the interface is flat and the height fluctuations are such that the height correlation of two points at a distance $\mathbf{r}$:

$$G(\mathbf{r}) \equiv \langle (h(\mathbf{r}+\mathbf{r_o}) - h(\mathbf{r_o}))^2 \rangle \qquad (98)$$

is finite. At or above T_R however, the interface is rough and G diverges as $r \to \infty$. The renormalization group theory produces a logarithmic divergence. Below T_R the height differences fluctuate logarithmically only at short distances, below a correlation length ξ, but remain finite above ξ:

$$G(r) \sim \ln(r) \text{ for } r < \xi \text{ and } G(r) \sim \ln(\xi) \text{ for } r > \xi \qquad (99)$$

The correlation length diverges at T_R as:

$$\xi \propto e^{\frac{C}{\sqrt{T_R - T}}} \qquad (100)$$

At this point the energyof a step is $\sigma\xi$ which should be of the order kT. Therefore:

$$\beta \sim \xi^{-1} \sim e^{-\frac{C}{\sqrt{T_R - T}}} \qquad (101)$$

This singularity is an essential one, since all the derivatives of any order vanish at T_R but there is no divergence in the specific heat.